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OCA PAD INITIATION - PROJECT HEADER INFORMATION

08/12/88

Active

Project #: E-18-656
Center # : R6363-1A0

Cost share #:
Center shr #:

Rev #: 0
OCA file #:
Work type : RES
Document : GRANT
Contract entity: GTRC

Contract#: 5 R01 DE07754-03
Prime #:

Mod #:

Subprojects ? : N
Main project #:

Project unit: AE Unit code: 02.010.110
Project director(s):
MAREK M I MAT ENGR

Sponsor/division names: DHHS/PHS/NIH / NATL INSTITUTES OF HEALTH
Sponsor/division codes: 108 / 001

Award period: 880801 to 890731 (performance) 891031 (reports)

Sponsor amount	New this change	Total to date
Contract value	134,475.00	134,475.00
Funded	134,475.00	134,475.00
Cost sharing amount		0.00

Does subcontracting plan apply ? : N

Title: DISTRIBUTION OF MERCURY FROM DENTAL AMALGAMS

PROJECT ADMINISTRATION DATA

OC contact: Faith Gleason 894-4820

Sponsor technical contact

Sponsor issuing office

G.G. ROUSSOS, PH.D., CHIEF, CARIES &
(301)496-7884
RESTORATIVE MATERIALS RESEACH BRANCH
NATL INSTITUTE OF DENTAL RESEARCH
BETHESDA, MD 20892

THERESA RINGLER, GRANTS MGT OFFICER
(301)496-7437
EXTRAMURAL PROGRAMS, NIH/NIDR
BETHESDA, MD 20892

Security class (U,C,S,TS) : ONR resident rep. is ACO (Y/N): N
Defense priority rating : supplemental sheet
Equipment title vests with: Sponsor GIT X
NO EQUIPMENT MAY BE PURCHASED IN THE LAST 6 MONTHS OF THIS GRANT PERIOD

Administrative comments -
INITIATION. 3RD YEAR OF GRANT.

X Reports Coordinator (OCA)
X GTRC
X Project File
2 Contract Support Division (OCA)
 Other

that evaporates from the liquid depends on the kinetics of the individual processes involved (transport, redox reactions, evaporation from the solution), which have not been investigated. Finally, it is important to determine the repassivation characteristics of various amalgams which determine the duration of the transients and thus control the amount of mercury released during a transient.

When the quantitative description of the release process is available and the roles of the fundamental variables are determined, it may be necessary to reexamine in more detail some of the possible accelerating factors, such as galvanic and crevice conditions, and the effects of additional environmental variables. If time allows some of these studies would be included in the proposed program, but generally they would be subjects of future programs.

C. PROGRESS REPORT

Performance dates: 08/01/86 through 7/31/89

Key Personnel:

Dr. Miroslav I. Marek (PI)
Professor

Dates of service: 08/01/86 through 7/31/89
35% appointment to this project

Summary of Specific Aims:

The proposed Specific Aims included determination of the dissolution rates from dental amalgam phases and dental amalgams, determination of the form of dissolved mercury, exploration of the effects of the components of the environment, and exploration of the effects of temperature, galvanic coupling, crevices, oxygen concentration and abrasion.

The following changes in the Specific Aims have been made:

- a. Postponement of the study of the effect of temperature until the next funding period.
- b. Deletion of the study of the effects of the components of the environment for lack of time.
- c. Addition of an analysis of the overall mechanism of the mercury release.
- d. Addition of a study of evaporation of mercury from solutions.
- e. Addition of a study of the methodology of determination of mercury dissolution rates.

Results:

In retrospect, it is obvious that the original program was overly ambitious and the difficulties were underestimated. Although the Specific Aims will be accomplished with only a few exceptions, it was impossible to do the studies in the depth they would have deserved, and some of the major parts of the program had to be postponed until the third project year. Also, publication of many of the results had to be delayed until the interpretation of the results becomes sufficiently clear. There were three major reasons for the slowness of the progress in achieving the Specific Aims:

1. The complexity of the chemistry and electrochemistry of mercury.

Although a substantial literature review and preliminary work were performed in preparation of the previous proposal, some of the complexities appeared only after the initiation of the program since very little literature deals specifically with the investigated conditions. Mercury dissolves in both ionized and nonionized state, the ionic dissolution from dental amalgam requiring the presence of complexing agents. There are, however, complex reduction/oxidation reactions which cause oxidation of nonionized mercury, and disproportionation of ionized mercury into a higher oxidation form and nonionized form. Moreover, bacterial action enhances the reduction into the nonionized form. Since the nonionized form is volatile, the reactions are of great importance both for the understanding of the mercury release in vivo and for the methodology of testing. The interpretation of the initial results in which these reactions have not been controlled or understood has consumed a considerable project time. The realization of the complexities of the process has lead to the addition of a Specific Aim dealing with the overall mechanism of the mercury release, and another one to examine the evaporation of mercury from solutions.

2. Problems in methodology of testing.

The proposed program was based on the testing methodologies reported in the literature, and the preliminary tests. These revealed neither the substantial sources of error related to the losses of mercury during dissolution experiments, other than those due to absorption, nor the effects of dissolved mercury concentration on the mercury dissolution rate which play a role in the determination of the dissolution rate as a function of time. New methodology had to be developed to deal with the problems, and a new Specific Aim was added to address this question.

3. Equipment failures

The most important piece of the analytical equipment for this research, the Atomic Absorption Spectrophotometer, is about 15 years old and has been suffering from frequent breakdowns.

SPECIFIC RESULTS:

(The order of discussion follows the actual timetable of the program rather than the original list of Specific Aims)

1. A study of evaporation of mercury from solutions. (New Specific Aim)

The study was performed to explain the losses of mercury from solutions during testing. Mercury was dissolved under nonoxidizing conditions in distilled, deionized, filtered, and sterilized water, in water treated with a bacteriocidal agent, and in a sodium chloride solution. Mercury loss by evaporation was monitored. The results showed that in long-term tests the bacteria, which were present in non-sterilized solutions, strongly affected the evaporation rate. The time dependence of evaporation was attributed to the kinetics of bacterial growth, and the effect of bacteria on evaporation to the disproportionation of the ionic mercury.

Significance: The significance of the results is two-fold: for the methodology of testing they showed the importance of using sterilized solutions if conditions are suitable for unwanted bacterial growth, and/or to prevent or take into account volatilization of mercury. For the mercury release in vivo the

results showed that the bacterial activity may play a role in the mechanism, contributing to the presence of mercury in the oral atmosphere.

2. An analysis of the general mercury release mechanism for dental amalgam restorations.
(New Specific Aim)

A theoretical analysis was performed to identify the possible processes involved in the mercury release and to select the most likely model as a basis for future research. A dry evaporation, dissolution, and dissolution/evaporation models were considered. The dissolution/evaporation model was selected as best conforming to clinical observations. The individual processes, including transports in solid and liquid phase, interface reactions, redox reactions, and evaporation were identified. The model is shown schematically in Fig. 1 on Page 30.

Significance: The model provides a description of the overall mechanism and a focus for the research. The selected model shows the importance of identifying the rate controlling process, which has become one of the main aims of the new proposed program.

3. A study of the effect of concentration on the results of the mercury dissolution tests.
(New Specific Aim)

As a part of the evaluation of the methodology of testing, the dissolution rates were determined as a function of a preexposure in the same type of solution (synthetic saliva and distilled water), with a minimal delay between the exposures. The containers were sealed to prevent losses by evaporation. The dissolution rates after the preexposure were consistently higher than the average rate during the preexposure, in spite of the reported (and also observed in this research) decrease in the dissolution rate with time. The results were interpreted as the effect of concentration of the dissolved mercury on the dissolution rate. In the follow-up study the relationship was mathematically formulated and a method for correcting the data was suggested (see Appendix B).

Significance: Together with the evaporation losses the concentration effect is thought to be responsible for the extremely wide dispersion of the dissolution rate data reported in the literature [17]. The correction procedure allows to obtain accurate values of the fundamental dissolution parameters, such as the initial and steady state rate and the time constant.

4. A study of the effect of composition of the gamma-1 phase of dental amalgam on the mercury dissolution rate.
(Part of the original Specific Aim #1)

The effect of the mercury/silver ratio and tin content in the gamma-1 phase on the mercury dissolution was studied under open-circuit conditions. A special cell was used to allow the evaluation of the fundamental dissolution parameters, using the correction procedure described above. The results show that the Hg/Ag ratio had little effect on the Hg dissolution rate except when it approached the phase boundary with liquid Hg, in which case the dissolution rate sharply increased. The tin content had a strong influence on Hg dissolution; both the initial and stabilized dissolution rate decreased with increasing tin content, and the time constant of the dissolution rate decay decreased (see Appendix). The effect of tin was attributed to the formation of a passive film which is a major barrier against mercury dissolution.

Significance: The formation of a passive film of tin and its effect on the mercury dissolution rate help explain both the observed decreasing rate of dissolution with time in vitro, and the clinical observation of mercury vapor in the oral atmosphere following chewing [4,5,15,16]; the abrasion associated with chewing mechanically disturbs the passive layer and thus enhances dissolution, which is then followed by evaporation. The results confirmed the previously reported, but also disputed presence of dissolved tin in the gamma-1 phase of dental amalgam. They were in agreement with the reported similar effect of an air-formed film on mercury evaporation from dental amalgam [30,31]. Because of the strong effect of tin on the mercury release a detailed study of abrasion and repassivation was included in the new proposed program.

5. A study of the partition of dissolved mercury into ionized and nonionized forms.

(Original Specific Aim #2)

The study was performed by dissolving mercury from dental amalgam into synthetic saliva in a special cell, sampling the solution and processing portions of the sample in two ways: 1) stabilizing the solution and then analyzing it by the standard cold-vapor AAS technique; 2) introducing the solution immediately into AAS without stabilization. The former procedure showed the total dissolved mercury content, while the latter showed only the volatile, nonionized mercury. The difference represented the ionized mercury. The results have shown the presence of both forms of Hg, the nonionized mercury reaching an almost constant value (about 50 ppb) for all experimental conditions, but at a rate varying with the material. The total mercury concentration, on the other hand, continued to increase with time, and the results were similar to those obtained in the study (4) above. To date the tests have been performed under open-circuit conditions; the evaluation of the effect of the electrode potential is a part of the work in progress.

Significance: Since the clinically most significant form of released mercury is the vapor in the oral atmosphere, the partition and its changes is of great importance. The results have shown conclusively that ionized mercury is present in the solution in spite of the thermodynamic difficulty of directly dissolving mercury in pure water. Most of the ionized mercury seems to result from the redox reactions in the liquid. This emphasizes the importance of studying the kinetics of the individual processes of the dissolution/evaporation model, as described in the new proposed program.

6. The effects of galvanic coupling, crevice conditions, and oxygen concentration cells on mercury dissolution.

(Part of the original Specific Aim #4)

Galvanic coupling: The corrosion effects of galvanic coupling are essentially due to a change in the corrosion potential caused by the contact with another metal. Therefore, a definitive evaluation of the effect will be possible only after the completion of the study of Hg dissolution as a function of the potential. Preliminary experiments were performed using amalgam/gold galvanic couples in dissolution tests performed as in (3) above. A 1.5-2x higher initial dissolution rate was observed for the galvanic couples. It has been realized, however, that the gold in the cell may have trapped some of the dissolved mercury.

Significance: The significance of galvanic contacts for mercury dissolution will be more apparent after the conclusion of the study of the effect of the electrode potential.

Crevice conditions: The effect of crevices on mercury dissolution was tested in two ways: (a) The amalgams were exposed to a solution simulating crevice

chemistry, i.e., high acidity and chloride concentration; (b) An artificial crevice was created on the surface of the dissolution specimen by covering part of the surface with a nonmetallic sheet. In the tests (a) a definite increase in the mercury dissolution rate (by an order of magnitude) was observed. This was attributed to the destruction of the passive film on the gamma-1 phase, which is the main barrier against mercury dissolution under static conditions. In the tests (b), however, only a modest increase (up to about 25%) in Hg dissolution was observed in short term tests, although a definite evidence of crevice corrosion was detected when the cell was disassembled.

Significance: Crevice conditions are a major cause of accelerated corrosion of dental amalgam, and the conditions in a crevice also result in an accelerated release of mercury. However, since the very mechanism of crevice corrosion is based on the restriction of transport of species into and from the crevice, the emission of dissolved mercury from the crevice into the bulk environment also is restricted. The crevice conditions between the tooth and a restoration are likely, however, to be responsible for the release of mercury into the dental tissues, and possibly through them into the circulation system. This question will have to be examined further in future research. Also to be examined is the effect of corrosion conditions under a biofilm, which may lead to an increased mercury concentration in the film and consequent accelerated mercury release.

Oxygen concentration: Extensive tests were performed to compare the mercury dissolution rates in the presence and absence of dissolved oxygen. In all cases the presence of oxygen substantially increased the dissolution rate. The effect was attributed to the oxidation reactions in the liquid which convert the nonionized mercury into the oxidized form and thus allow further fast dissolution of nonionized mercury. A possible additional effect of the potential difference associated with the oxygen concentration will be evaluated later.

Significance: The results show that the mere decrease in oxygen concentration, e.g., under the biofilm, is not responsible for accelerated mercury dissolution. Only the other chemistry changes, such as acidification, which directly affect the stability of the protective film, also cause an increased rate of mercury dissolution.

7. A study of the effect of abrasion-corrosion on mercury dissolution.
(Part of the original Specific Aim #4)

Abrasion test were performed using a special cell described previously [32], in which rotating abrasion pads were pressed against the specimen surface, removing the surface film. Concentration of mercury in the solution was periodically determined and compared with the concentration after a static exposure. The results showed a substantial increase in the average dissolution rate, reaching two orders of magnitude. Although an increase was observed for both tin-free and tin-containing gamma-1 phase, the difference from the static exposure was much higher for the tin-containing material. The increase for the tin-free phase has been attributed to the deformation of the surface layer which caused a phase change and appearance of a small amount of liquid mercury on the surface. For the tin-containing phase the additional increase in the mercury dissolution rate has been attributed to the destruction of the tin oxide surface film, which is a major barrier against mercury dissolution under static conditions.

Significance: The results are in agreement with the reports for dry evaporation [30,31] and with the clinical observation of mercury in the oral atmosphere after chewing [4,5,15,16]. They indicate the importance of performing a detailed study of the kinetics of mercury dissolution during and after abrasion

and of the repassivation characteristics of various dental amalgams which may control the amounts of mercury released in vivo.

8. The effect of the electrode potential on the mercury dissolution rate.
(Original Specific Aim #1)

Although this study was planned as the initial one in the program for the reported period, substantial modification of the experimental design was found necessary. The investigation was postponed to the third year and is now in progress. In addition to the general reasons explained at the beginning of this report the following was the cause of the delay: When tests were initiated as originally planned, the results were inconsistent; large differences were found between the electrochemical parameters (integrated current) and the analytical data for all the elements involved. The concentration of mercury in the solution was lower than expected, in spite of the fact that nonionic mercury should have made the concentration higher than calculated. The discrepancy was traced to the presence of the auxiliary platinum electrode in the cell; since the electrode is driven by the potentiostat to a potential different from that of the specimen to achieve the potential control, the dissolved mercury often plates out on the platinum and is not included in the analysis. Since the potential of the platinum is not monitored and varies depending on many factors, the amount is not consistent and correction are difficult. Although the plated out mercury can be stripped, the amount determined, and included in the result, this procedure also is not satisfactory. As the electrode traps some of the mercury, the amount of mercury in the solution decreases, which affects the dissolution rate. Since the changes are not consistent, it is not possible to correct for them. The procedure also would make it impossible to perform uninterrupted tests with periodic sampling of the solution.

Extensive experiments were performed to avoid the problem. In the new design the auxiliary electrode is placed in a separate compartment connected to the main cell via a membrane and a gel salt bridge. Although some mercury loss still occurs, the amount is much lower than before and corrections can be made. The work is in progress and is expected to be concluded by the end of the reported program period.

Publications:

E. Euvrard: "Dissolution and Evaporation of Metallic Mercury from Aqueous Solutions." M.S. Thesis (supervised by M. Marek), Georgia Institute of Technology, Atlanta, GA, 1987. The results also will be incorporated in future publications.

M. Marek: "Dissolution and Evaporation of Mercury from Dental Amalgam." IADR Paper #42, DMG Microfilm, 1987.

M. Marek: "Mercury Dissolution from the Gamma-1 Phase of Dental Amalgam." IADR Paper #33, DMG Microfilm, 1988.

M. Marek: "The Release of Mercury from Dental Amalgam: Mechanism and in vitro Testing." Submitted to the Journal of Dental Research.